wafer scanning machines in an IBM resist ER1, which is a formulation of the diazonaphthoquinone-novolak type, similar to AZ 2400. Note in all cases - Figs. 4.1, 4.10 and 4.11 - the excellent images with near-vertical wall profiles. In addition, in all mid-UV resists, it was also determined that little or no reciprocity failure takes place in 308-nm excimer laser exposures at doses of lithographic interest. Thus, it may be asserted that from the point of view of lithographic imaging, the behavior of the above mid-UV resists is essentially the same under excimer laser and Hg-lamp illumination. The reciprocity behavior of the resist process, including its lithographic, optical, and photochemical aspects, is discussed at length in Sec. 6.4.

6.2. RESISTS FOR EXPOSURE AT 248 NM

A large number of chemical formulations have been investigated as possible photoresist candidates for illumination with deep UV wavelengths in the ~250-nm region, particularly with the 248-nm KrF laser. The comprehensive picture that emerges from these studies is that the overall photoresist situation for 248-nm exposure is significantly different from that for 308-nm exposure. The primary differences between deep UV and mid-UV excimer laser exposures of resists arise from the differences in their optical and photochemical behaviors in the two spectral regions. The performance of most of the commercially available resist materials is considered unacceptable at deep UV wavelengths due to certain fundamental shortcomings exhibited by them: resists that have good plasma-etching resistance show excessive unbleachable absorbance, whereas those with better transmission characteristics have inadequate etching resistance. In a photoresist with high deep UV absorbance that does not bleach, as in the well-known diazonaphthoquinone-novolak systems, the light exposure intensity received near the bottom of the resist layer is much smaller than that near the top; this invariably produces overcut image profiles with sloping walls. Consequently, although deep UV projection lithography systems can readily deliver image resolution in the

vicinity of 0.5 micron, the maximum resist thickness that one may use with conventional resists for deep UV exposure must be limited to below 0.5 micron. Such a resist thickness value is too low from two points of view: first, it provides inadequate coverage of the underlying topography on the wafer, and second, its etching resistance is poor. In the sections below we describe various categories of deep UV resists and the approaches investigated to overcome the limitations mentioned above.

6.2.1. Dissolution Inhibition Resists

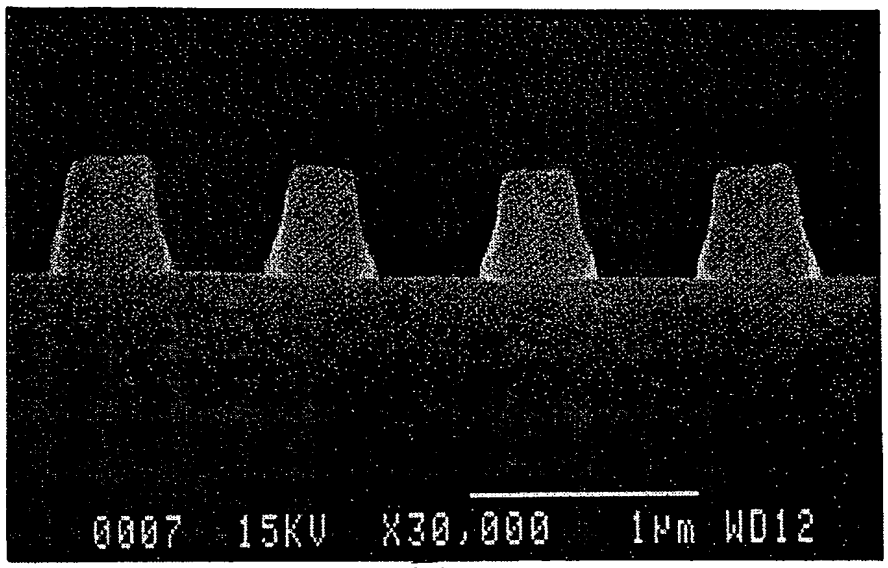
Exposures with the 248-nm KrF excimer laser in a variety of photoresists have been reported in contact printing mode [1-3,5,8,15,19,20,27,39,48], 1:1 full-wafer scanning projection printing mode, and in step-and-repeat projection printing mode [26,37,45-47,49,55-59,63, 65,68,70,72]. Some of these have been previously described in Secs. 4.1, 4.2.1, and 4.2.2. Examples of images contact-printed with a KrF laser in Shipley/AZ 2400, the most widely studied dissolution-inhibition deep UV resist system, are shown in Fig. 4.2 [1]. These images were produced in 1-micron-thick resist with an exposure dose of 125 mJ/cm^2. The expected sloping wall profiles are clearly seen in these scanning electron micrographs. Patterns printed by projection lithography systems exhibit even greater slopes. Some examples of projection images obtained in AZ 2400 are given in Figs. 4.12, 4.17 [7] and 4.25 [57]. As mentioned in the preceding paragraph, the wall slopes can be improved by using thinner resist layers; further, overexposure also helps in making the profiles more vertical. This is illustrated in Fig. 4.3, which shows contact-printing results in 0.4-micron-thick Shipley 2400-17 resist in which an exposure dose of 230 mJ/cm^2 was used [27].

Many other novolak-based and other dissolution-inhibition-type resist systems have been investigated for 248-nm excimer laser lithography. These include AZ 4050 [27] and 5214 [49], McDermid PR-1024MB [49], Hunt HPR 1182 [57], and Hitachi RD-2000N [49,57] and 5000P [27]. AZ 4050 is designed primarily for use at near UV

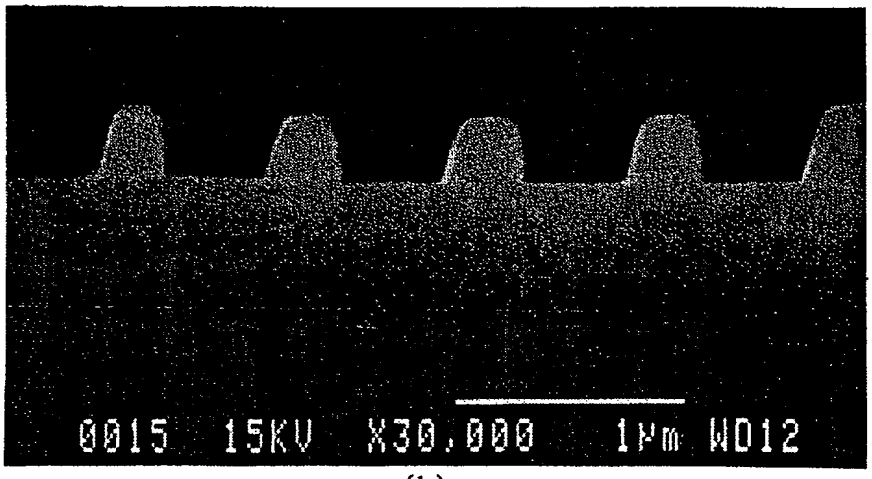
wavelengths and has higher absorbance than Shipley/AZ 2400 at 248 nm; it therefore exhibits image profiles of poorer slope characteristics. 0.5-micron line-space pairs produced in AZ 4050 by contact printing with a KrF laser are shown in Fig. 6.2(a) [27]. AZ 5214, Hunt HPR 1182, and McDermid PR-1024MB, although designed for different process conditions, have deep UV absorption properties similar to AZ 4050 and thus produce similar images in single-layer lithography experiments [49,57]. Hitachi RD-2000N, which consists of an azide sensitizer and a phenolic resin, also absorbs heavily at 248 nm, but since it is negative-acting, it produces undercut profiles [49, 57]. The formulation of the Hitachi 5000P resist is somewhat different from other novolak-based resists in that its base resin is pure para-cresol novolak, whereas the other novolak-based resists use various mixtures of ortho-, meta-, and para-cresols. The use of pure para-cresol novolak produces significantly higher transmission at 248 nm; however, this also leads to exposure energy dose requirements as high as 2 J/cm^2. In addition, the 5000P suffers from a high development rate in the unexposed regions, leading to poor image profiles. An example of contact-printed images in this resist is shown in Fig. 6.2(b).

6.2.2. Organosilicon Resists

The fundamental problem encountered in KrF laser exposure of the otherwise highly desirable positive photoresists with novolak resin and diazonaphthoquinone sensitizer is that, as discussed above, the deep UV absorbance of both of its components is high, typically >1 $micron^{-1}$, and does not bleach on exposure. Thus, a logical remedy to the above hurdle would be to seek a chemical formulation with greater transmission than novolak and diazonaphthoquinone in the deep UV. Some success has been achieved in this direction by Orvek et al., who have investigated a positive-acting organosilicon resist [48]. The base resin, PVPTMS, in this system is O-trimethylsilyl poly(vinylphenol), which is used with an organic sensitizer that acts through photogeneration of halogen acids that catalytically convert the PVPTMS in the exposed resist areas into a



(a)



(b)

Fig. 6.2 Scanning electron micrographs of patterns contact-printed with 248-nm excimer laser exposures: (a) 1.0-micron-pitch features in AZ 4050 resist and (b) 0.8-micron-pitch features in Hitachi 5000P resist. [From Ref. 27]

material with a significantly increased concentration of hydroxyl groups, making it more soluble in aqueous developers, as illustrated in Fig. 6.3. A comparison of the 248-nm transmission characteristics of the PVPTMS resist with those of two novolak-based Shipley resists - S2400, already discussed above, and S1400, a common g-line resist - is shown in Fig. 6.4(b). Note the markedly higher transmission of PVPTMS, which, as may be expected, should result in images with more vertical wall profiles than AZ 2400. An example is given in Fig. 6.4(a), which illustrates contact-printed images obtained in 1-micron-thick PVPTMS with 248-nm KrF laser exposure. Although these imaging characteristics appear satisfactory, this resist system is not close to being usable in a production environment, particularly due to problems associated with deposition of residue during development and postexposure chemical activity of the photogenerated acids. PVPTMS has also been used in a bilayer patterning scheme, which is discussed in Sec. 6.2.5.2.

6.2.3. Chain Scissioning Methacrylate Resists

Another class of positive-acting resist materials that have been studied extensively in the deep UV is the poly(methylmethacrylate) (PMMA) family of polymers. Two examples of such compounds are shown in Fig. 6.5. Upon absorption of deep UV and vacuum UV light, these materials undergo a chain scissioning mechanism, which leads to a reduction of their molecular weight and, as a result, to increased solubility in the exposed resist areas. Thus, photochemically, the methacrylate polymers function differently from the dissolution-inhibition-type resists such as the diazonaphthoquinone-novolak systems. Polymers in this class are characterized by good transmission in the deep UV, but are unacceptable for most production lithography applications because their plasma-etching resistance is insufficient. The optical transmission properties of PMMA and several modified methacrylate copolymers have been measured by Wolf et al. [39] and are shown in Fig. 6.6(a). These should be compared with the transmission curves for various conventional novolak-based resists, shown in

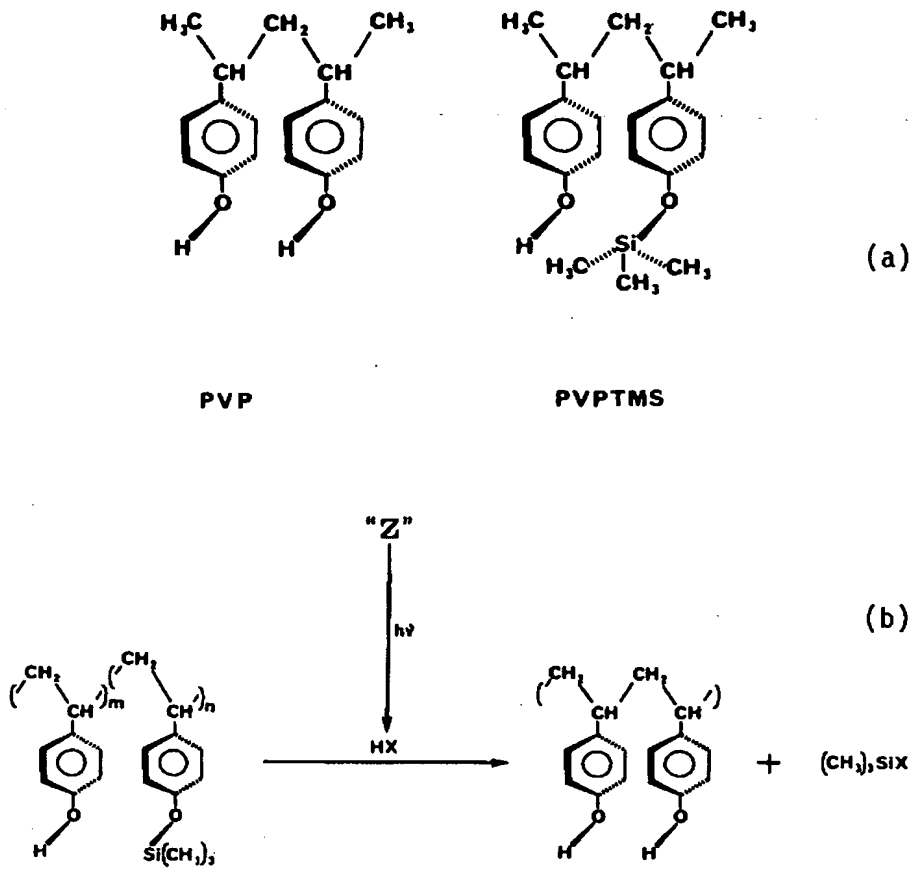
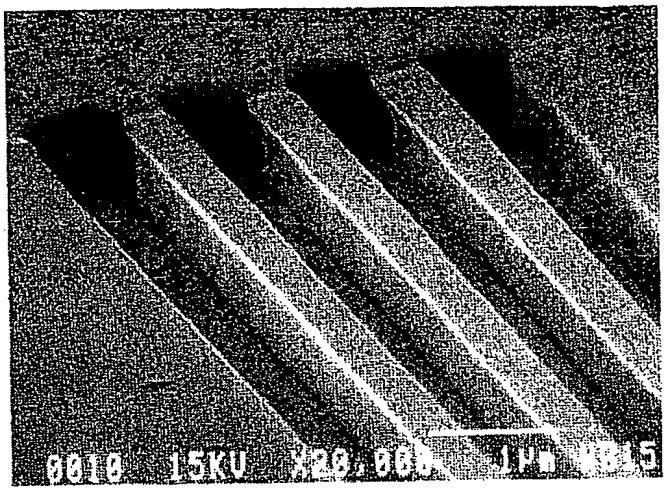
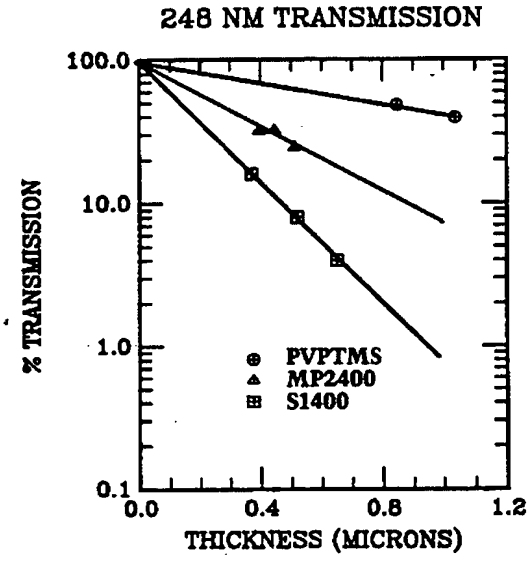


Fig. 6.3 (a) Structure of poly(vinylphenol) (PVP) and the organosilicon derivative O-trimethylsilyl poly-(vinylphenol) (PVPTMS); (b) catalytic decomposition of PVPTMS in the presence of photogenerated acid. [From Ref. 48]

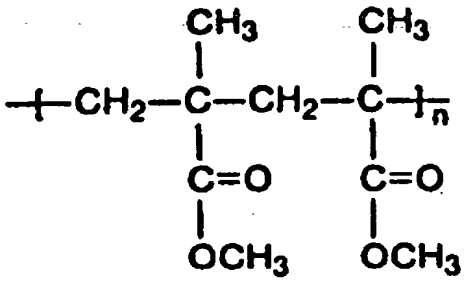


(a)

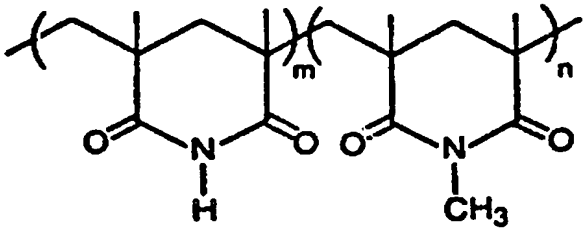


(b)

Fig. 6.4 (a) 0.5-micron images contact printed with 248-nm KrF excimer laser exposure in 1.0-micron-thick PVPTMS resist; (b) transmission of PVPTMS and Shipley S2400 and S1400 at 248 nm. [From Ref. 48]



(a)



(b)

Fig. 6.5 Structure of (a) poly(methylmethacrylate) (PMMA) and (b) poly(dimethylglutarimide) (PMGI).

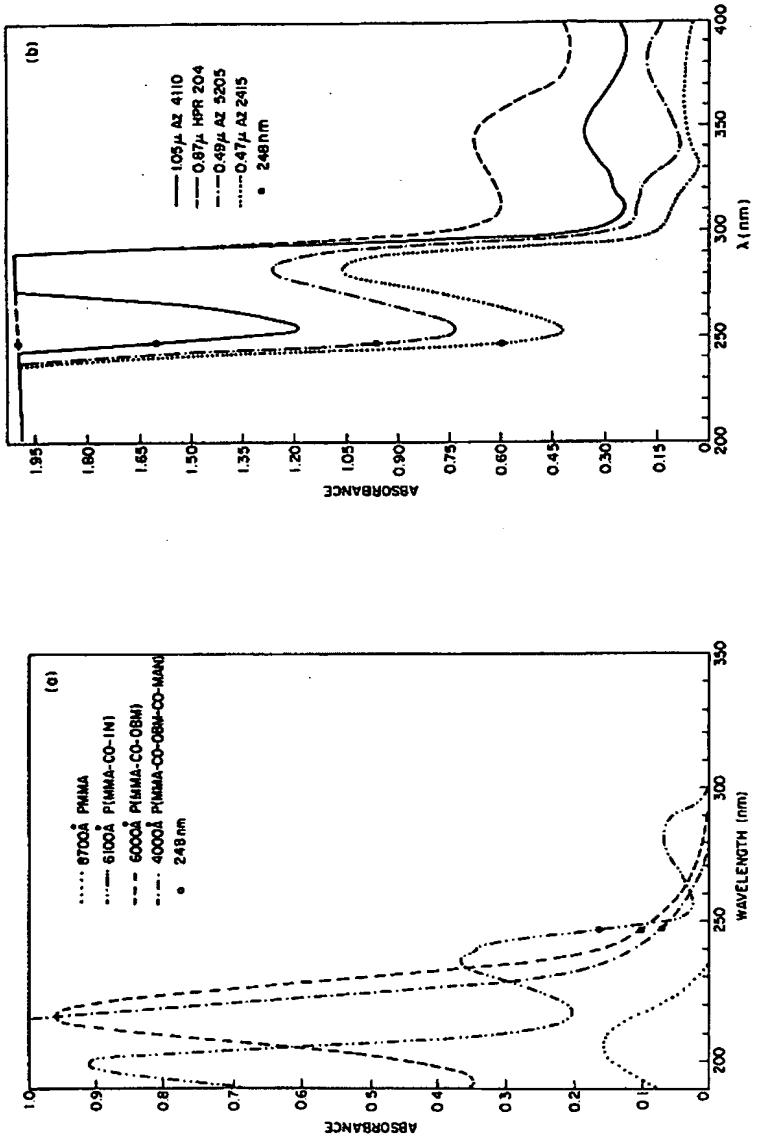
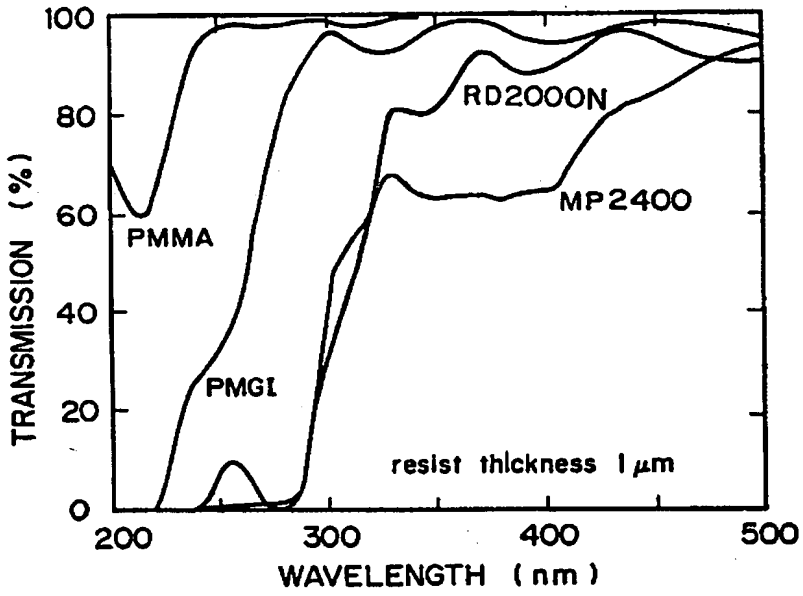


Fig. 6.6 UV absorbance spectra of several (a) methacrylate polymers and (b) novolak-based resists. [From Ref. 39]

Fig. 6.6(b). As the data in these figures illustrate, the absorbance values for the methacrylate resists are an order of magnitude lower than for the novolak-based systems. As a consequence, although resists of the PMMA family require very high exposure doses, they produce images with excellent profiles. In projection printing experiments on a 0.37-NA 248-nm achromatic step-and-repeat system, Nakase et al. [47] have reported an exposure dose requirement of 32 J/cm^2 for PMMA and 10 J/cm^2 for poly(dimethylglutarimide) (PMGI). Kameyama and Ushida [46], using an identical exposure tool, have patterned 0.55-micron-wide lines and spaces in 1-micron thick PMMA and demonstrated that it is possible to obtain near-vertical profiles in this resist in deep UV projection printing; some examples of their results are shown in Fig. 4.26. We summarize the above discussion of novolak-based and other dissolution-inhibition-type resists and methacrylate-based chain-scissioning-type resists in Fig. 6.7 [49] with a comparison of the dose sensitivities and imaging characteristics alongside the optical transmission spectra for MP 2400, RD-2000N, PMMA, and PMGI.

6.2.4. Chemical Amplification Resists

Recent investigations in deep UV resist systems have directed attention toward chemical amplification as a means of achieving both high sensitivity and high resolution in single-layer patterning [63,65]. An IBM experimental deep UV resist, XPR, based on chemical amplification has been described recently by Woods et al. [63]. In this system, a photoactive precursor, on absorption of deep UV photons, undergoes decomposition and produces an acid. During a postexposure bake step, this photogenerated acid increases the solubility of a resin in aqueous alkaline developers, thus producing positive-tone images. In the presence of heat, the acid acts on the resist in a catalytic fashion. Thus, such a resist system is capable of exhibiting high sensitivities; exposure dose requirements as low as 10-20 mJ/cm^2 have been experimentally observed. The resin in XPR has an aromatic content, which gives the resist good plasma-etching resistance as well as good



Resist	$\alpha_{248}(\mu m^{-1})$	Sensitivity (J/cm^2)	0.4μm L/S
PMMA	0.08	32	
PMGI	0.58	10	
MP2400	2.74	0.1	
RD2000N	3.25	0.1	

Fig. 6.7 Comparison of absorption, exposure dose sensitivity, and imaging characteristics of PMMA, PMGI, MP2400, and RD2000N resists. [From Ref. 49]

thermal stability. In addition, the low (0.2 micron^{-1}) deep UV absorbance of the resin permits use of resist layers of convenient thicknesses ($\sim$1 micron). Woods et al. [63] have carried out an extensive lithographic evaluation of XPR on a 0.35-NA monochromatic step-and-repeat system. As an example, 0.5-micron-wide lines and spaces with vertical wall profiles obtained in 0.85-micron-thick resist are shown in Fig. 6.8.

Another chemical-amplification-based resist system has been recently developed for commercial availability in a joint effort between the Shipley Company and the Rohm and Haas Company [65]. This negative-tone resist, called XP-8843, consists of three components: a base resin, poly(p-vinyl)phenol, chosen for its low deep UV absorbance (0.17 micron^{-1}), good resistance in plasma etching, and solubility in an aqueous base; a photosensitive acid generator; and a melamine crosslinking agent. Absorption of deep UV light causes photolysis of the photosensitive component to produce an acid; when this is followed by a postexposure bake step at 110-150 °C, a catalytic reaction takes place between the resin and crosslinking agent resulting in a resist film that is highly crosslinked in the exposed regions. The greatly reduced solubility of the crosslinked resist areas in an aqueous developer, thus, produces negative-tone images. The above process flow is illustrated in Fig. 6.9 [65]. A detailed lithographic investigation of XP-8843, encompassing its optical, chemical, and thermal aspects, has been reported by Thackeray et al. [65]. The projection images in this study were printed on a 0.35-NA monochromatic step-and-repeat tool. Figure 6.10 shows 0.5-micron line-space features obtained in a 1-micron-thick resist film with a nominal dose of 16 mJ/cm^2. Note the near-vertical image profiles and the large exposure dose latitude.

We remark that whereas resist systems based on chemical amplification schemes appear attractive from the points of view of dose sensitivity, image profiles, and plasma-etch resistance, they also have the drawback of requiring the extra postexposure baking step. The latter may also be a potentially sensitive step, in

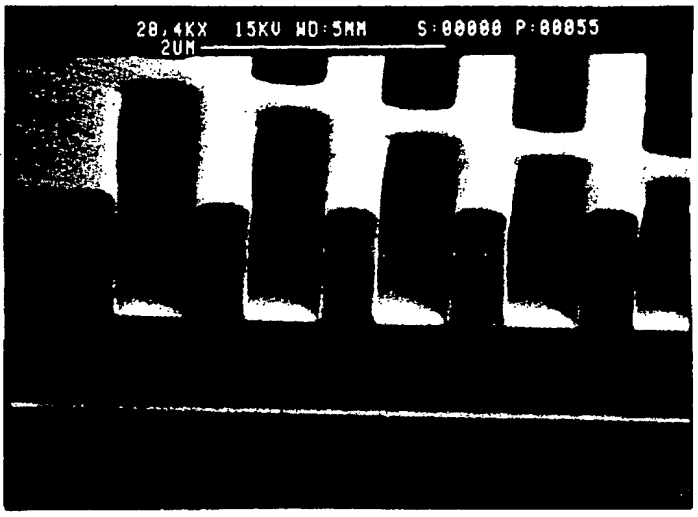


Fig. 6.8 Images with 0.5-micron line-space features obtained in 0.85-micron-thick chemical-amplification resist XPR with 248-nm excimer laser exposure on a 0.35-NA step-and-repeat system with a monochromatic lens. [From Ref. 63]

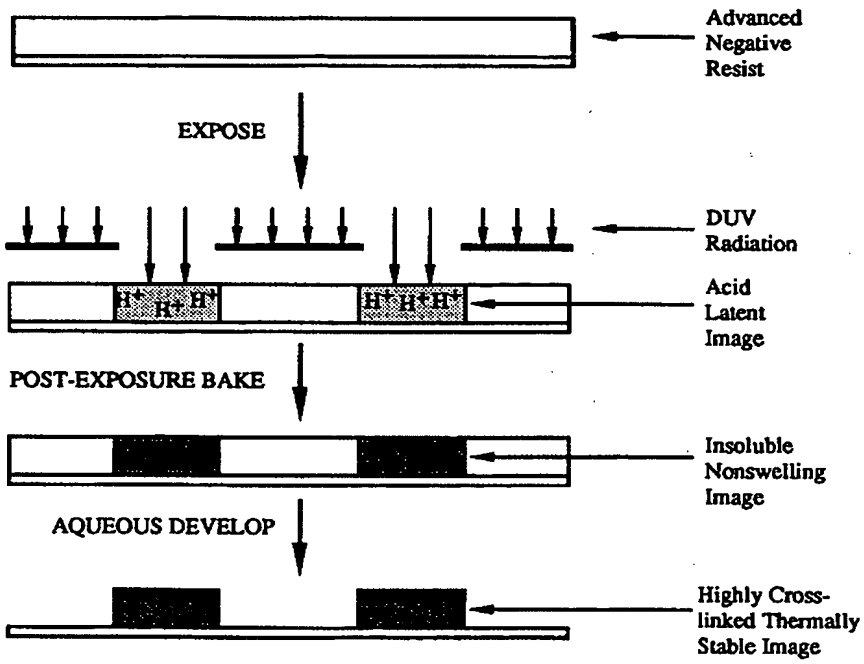


Fig. 6.9 Process flow for the Shipley XP-8843 deep UV chemical-amplification resist. [From Ref. 65]

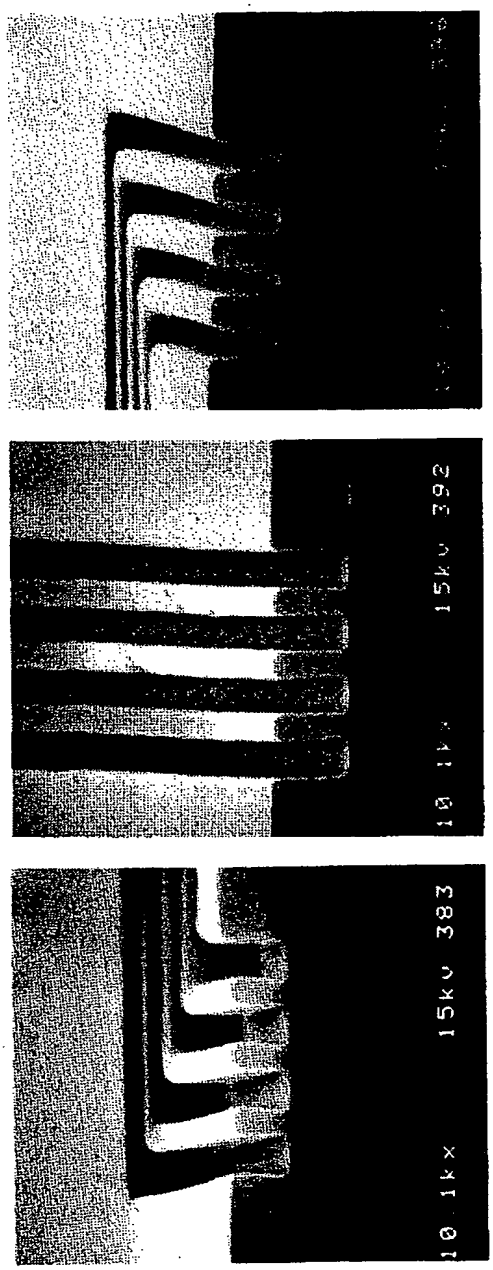


Fig. 6.10 0.5-micron images obtained in 1-micron-thick XP-8843 resist on a 248-nm KrF excimer-laser stepper with a 0.35-NA monochromatic lens. The wafers were exposed with (a) 26 mJ/cm^2, (b) 30 mJ/cm^2, and (c) 34 mJ/cm^2, and post-exposure baked at 140 °C for 1 min. [From Ref. 65]

that the dependence of the resist performance on it is critical. It is expected that with more extensive experimentation and a larger performance evaluation data base obtained in production applications, a better understanding of the key resist parameters will emerge.

6.2.5. Multilayer Resist Systems

In view of the various limitations of the deep UV resists described above in single-layer production lithography applications, there has been a sizeable and ongoing effort in development of multilayer systems. Although multilayer patterning clearly adds to wafer fabrication costs due to numerous additional process steps, its attractiveness arises not only from its ability to produce high-resolution image profiles with large aspect ratios, but also from the fact that it potentially overcomes the fundamental depth-of-focus limitation of optical lithography tools in single-layer imaging. The importance of the depth-of-focus advantage increases as the imaging wavelength decreases. Thus, whereas in conventional UV and mid-UV lithography the greater depth of focus offered by multilayer patterning is a luxury one may decide not to have in view of the added cost, in deep UV lithography many users view it as an alternative that is very viable when the overall economic considerations of the lithography process steps in the wafer fabrication cycle are taken into account. Further, in excimer laser lithography at the shorter wavelengths of 193 nm and 157 nm, which are beginning to be investigated for image resolution in the 0.25-micron regime, it is likely that the use of multilayer resist systems will become the preferred, if not required, approach to pattern formation.

6.2.5.1. Trilevel Resist Structures

A very common multilayer resist system consists of a three-layer structure: a top layer, <0.5-micron thick, for imaging; a middle layer, $\sim$0.1-micron thick, as an etch barrier; and a bottom layer, >1.0-micron thick, into which the patterns are transferred by dry etching. Using a 248-nm excimer laser stepper,